

PATENT ABSTRACTS OF JAPAN

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(54) VINYLIDENE FLUORIDE COATING COMPOSITION

(57)Abstract:

PURPOSE: To obtain the composition excellent in solvent resistance, boiling resistance and stain resistance by mixing a vinylidene fluoride polymer containing a crosslinking functional group, a vinyl polymer and a curing agent.

CONSTITUTION: The composition is obtained by mixing: 10-99wt.% vinylidene fluoride polymer (A) containing a crosslinking functional group, wherein the crosslinking functional group preferably comprises a hydroxyl group (hydroxyl number: 0.1-400mgKOH/g.dry) and which has a number-average molecular weight of preferably 1,000 to 150,000 and is prepared by copolymerizing vinylidene fluoride with a monomer containing a crosslinking functional group (e.g. 2-hydroxyethyl vinyl ether); 1-90wt.% vinyl polymer (B) preferably containing 10-100wt.% (meth)acrylic acid (ester) and preferably having a hydroxyl number of 0.1-400mgKOH/g.dry and a number-average molecular weight of 1,000 to 150,000; and a curing agent (C) comprising, e.g. an isocyanate compound in an amount of 0.05-20 times the mols of the hydroxyl groups of components A and B.

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CLAIMS

[Claim(s)]

[Claim 1] The fluoride vinylidene system paint constituent which serves as a fluoride vinylidene system polymer (A) containing a cross-linking functional group, and a vinyl system polymer (B) from a curing agent (C).

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the fluoride vinylidene system paint constituent excellent in solvent resistance, boiling-proof nature, and resistance to contamination. In detail, the fluoride vinylidene system polymer in a constituent is made to contain a hydroxyl group, and the paint constituent which constructs a bridge using a curing agent is offered.

[0002]

[Description of the Prior Art] Conventionally, although a fluoride vinylidene system paint is a paint characterized by maintenance-free one excellent in weatherability, since it does not have the bridge formation machine in which crosslinking reaction is possible, it has the fault in which the solvent resistance of the obtained paint film is inferior after dryness. Especially the air drying thing had the problem on which surface gloss disappears, when the dirt which bridge formation assembled to eye an inadequate hatchet for the works line paint use (low, moderate temperature forced drying) on the spot even if paint was possible, and sometimes adhered was wiped off by lacquer thinner etc.

[0003]

[The technical problem which is going to solve invention] As a result of inquiring wholeheartedly to the above-mentioned problem, by introducing functional groups, such as a hydroxyl group, into a fluoride vinylidene system polymer, and using a curing agent together, also by ordinary temperature dryness, the solvent resistance and boiling-proof nature of a paint film used to be improved, and that the resistance to contamination in real exposure is good used to make us clear as compared with the further usual fluoride vinylidene system paint, and we used to result in this invention.

[0004]

[Means for Solving the Problem] this invention offers the fluoride vinylidene system polymer (A) containing a cross-linking functional group, (it being called (A) component below), a vinyl system polymer (B), and the fluoride vinylidene system paint constituent that consists of a curing agent (C). The fluoride vinylidene system polymer (A) used for this invention is a fluorine polymer which contains a cross-linking functional-group machine for a fluoride vinylidene to monomer composition of a polymer, including 5 % of the weight or more. There is the method of carrying out copolymerization of a fluoride vinylidene and the monomer containing a cross-linking functional group as a method of making a fluoride vinylidene system polymer containing a cross-linking functional group in this invention. In this invention, a hydroxyl group, a carboxyl group, the amino group, an epoxy group, etc. can be mentioned with a cross-linking functional group.

[0005] As a monomer containing the hydroxyl group in which a fluoride vinylidene and copolymerization are possible For example, 2-hydroxyethyl vinyl ether, 3-hydroxypropyl vinyl ether, 2-hydroxypropyl vinyl ether, a 4-hydroxy butyl vinyl ether, A 3-hydroxy butyl vinyl ether, 2-hydroxy-2-methylpropyl vinyl ether, The vinyl ether; 2-hydroxy ethylene allyl-compound ether containing hydroxyl groups, such as 5-hydroxy pentyl vinyl ether or 6-hydroxy hexyl vinyl ether 3-hydroxypropyl allyl-compound ether, 2-hydroxypropyl vinyl allyl-compound ether, The 4-hydroxy

butyl BINIRUARIRU ether, the 3-hydroxy butyl allyl-compound ether, Allyl-compound ether containing hydroxyl groups, such as the 2-hydroxy-2-methylpropyl allyl-compound ether, the 5-hydroxy pentyl allyl-compound ether, or the 6-hydroxy hexyl allyl-compound ether; Crotonic-acid hydroxyethyl, Crotonic-acid 2-hydroxyethyl, crotonic-acid 2-hydroxypropyl, Crotonic-acid 3-hydroxypropyl, crotonic-acid 3-hydroxy butyl, Crotonic-acid 4-hydroxy butyl, a crotonic-acid 5-hydroxy pentyl, Or crotonic-acid hydroxyalkyl, such as a crotonic-acid 6-hydroxy hexyl; 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate, 2-hydroxy butyl acrylate, The acrylic ester and metallyl acid ester containing hydroxyl groups, such as 2-hydroxy butyl methacrylate or polyethylene-glycol methacrylate; A hydroxyethyl acrylamide, Although acrylamides and methacrylamide, such as hydronalium KISHIECHI methacrylamide, are mentioned, it is not necessarily limited to these. They are vinyl ether, allyl-compound ether, and crotonic-acid hydroxyalkyl preferably among the above-mentioned hydroxyl-group content monomers. As a monomer containing a carboxyl group, an acrylic acid, a methacrylic acid, a koro ton acid, a fumaric acid, an itaconic acid, etc. are mentioned, and an acrylamide and methacrylamide **** can mention glycidyl methacrylate, glycidyl acrylate, etc. as a monomer containing an epoxy group as a monomer containing the amino group.

[0006] Moreover, it is possible to copolymerize fluorine-containing monomers other than a fluoride vinylidene, for example, a fluoride vinyl, truffe RUORO ethylene, a tetrafluoroethylene, a bromotrifluoroethylene, a chlorotrifluoroethylene, pentafluoro ethylene, hexafluoropropylene or perfluoroalkyl, a truffe RUORO alkyl, truffe RUORO vinyl ether, etc. can be enumerated.

[0007] In this invention, a hydroxyl group is the most desirable as a cross-linking functional group. Preferably, 0.1 to 400 mgKOH/g-dry, the hydroxyl value of a hydroxyl-group content fluoride vinylidene system polymer is 5 - 100 mgKOH/g-dry still more preferably, and is 6 - 60 mgKOH/g-dry especially preferably. The number average molecular weight of these hydroxyl-groups content fluoride vinylidene system polymer is 5,000-20,000 preferably [it is desirable and] to 1,000-150,000, and a pan.

[0008] The vinyl system monomer which can be used for the polymerization of the vinyl system polymer (B) in this invention and (calling it (B) component hereafter) A methyl acrylate, an ethyl methacrylate, a butyl acrylate, methacrylic-acid butyl, Acrylic esters, such as acrylic-acid 2-ethylhexyl and methacrylic-acid 2-ethylhexyl, Anhydrides, such as carboxylic acids, such as a methacrylic ester, an acrylic acid, a methacrylic acid, an itaconic acid, and a fumaric acid, and a maleic anhydride, Epoxy compounds, such as glycidyl acrylate, diethylamino ethyl acrylate, Amino compounds, such as diethylamino ethyl methacrylate and aminoethyl vinyl ether, An acrylamide, methacrylamide, itaconic-acid diazido, alpha-ethyl acrylamide, A croton amide, a fumaric-acid diamide, a maleic-acid diamide, N-butoxy methylacrylamide, Amide compounds, such as an N-butoxy ethyl acrylamide, acrylonitrile, IMINORU methacrylate, styrene, an alpha methyl styrene, a vinyl chloride, vinyl acetate, a propionic-acid vinyl, etc. can be illustrated. It is [among these] desirable one sort or that an acrylic acid, an acrylic ester, a methacrylic acid, and two or more sorts of methacrylic esters are included preferably as a monomer component. Moreover, contents, such as the above-mentioned acrylic acid, an acrylic ester, a methacrylic acid, and a methacrylic ester, are 50 - 100 % of the weight still more preferably ten to 100% of the weight to a vinyl system polymer (B).

[0009] (B) As for a component, it is desirable to contain a hydroxyl group, and it is desirable to use acrylic-acid amides, such as methacrylic esters, such as methacrylic-acid 2-hydroxyethyl, methacrylic-acid hydroxypropyl, and acrylic-acid 2-hydroxyethyl, and acrylic esters or an acrylamide, and N-methylol acrylamide.

[0010] Although especially these hydroxyl-groups content monomer content is not limited, it is an amount which serves as 6 - 60 mgKOH/g-dry preferably especially five to 100 mgKOH/g-dry still more preferably 0.1 to 400 mgKOH/g-dry with a hydroxyl value to a vinyl system polymer (B). although especially the number average molecular weight of these vinyls system polymer is not ** limited -- desirable -- 1,000-150,000 -- it is 5,000-20,000 still more preferably

[0011] The rate of the fluoride vinylidene system polymer (A) which has the above-mentioned cross-linking functional group, and a vinyl system polymer (B) The (A) component is 99 % of the weight, and the 10 - (B) component is 1 - 90 % of the weight. usually, still more preferably (A) For the 30 - (B) component, the (A) component is [a component / the 60 - (B) component] 20 - 40 % of the weight 80% of the weight especially preferably one to 70% of the weight 99% of the weight (however, (A) component +(B) component =100 % of the weight). Moreover, to the above-mentioned (A) component and the (B) component, copolymerization of a adding-water resolvability silyl machine content monomer or the isocyanate content monomer may be carried out to both or either, and the polycondensation of the metal alkoxides, such as a silicon alkoxide, may be carried out to the hydroxyl group contained for (A) and/or the (B) component.

[0012] As a curing agent (C) in this invention, an isocyanate content compound or amino PURASUTSU compounds can be enumerated. As a typical thing of an isocyanate compound Tolylene diisocyanate, 4, and 4'-diphenylmethane diisocyanate, Xylylene diisocyanate, naphthylene G SOIANETO, a PARAFENI range isocyanate, Tetramethyl xylylene diisocyanate, hexamethylene diisocyanate, Dicyclohexylmethane diisocyanate, a lysine isocyanate, Hydrogenation xylylene diisocyanate, cyclohexyl diisocyanate, isophorone diisocyanate and the buret joint object of the above-mentioned isocyanate content compound, an isocyanurate joint object, and an adduct object are mentioned. Moreover, the block object of the above-mentioned isocyanate content compound is also illustrated. Moreover, you may add the organic-metal catalyst containing the amine catalyst for promoting the reaction of these isocyanates content compound and the hydroxyl group contained for the (A) component and the (B) component, tin, etc. Moreover, as an amino PURASUTSU compound, a melamine, a urea, benzoguanamine, etc. can be enumerated and methylol-izing or the thing which is further depended on fatty alcohol and which esterified is also further contained in these.

[0013] Although especially the addition of these curing agents is not limited, an isocyanate content compound is preferably added 0.6 to 2.0 times still more preferably 0.05 to 20 times to the number of mols of the hydroxyl group of the whole [(A) Component + (B) component] constituent. An amino PURASUTSU compound has 0.1 to 0.5 times preferably added still more preferably 0.001 to 20 times to the weight of the sum total of a (A) component + (B) component. An isocyanate content compound is ordinary temperature among these curing agents, the blocked isocyanate content compound is 100-180 degrees C, and, as for an amino PURASUTSU compound, it is desirable to add and use for the (A) component and the (B) component as a use which carries out dryness or printing dryness at the temperature of 130-200 degrees C. The fluoride vinylidene system paint constituent of this invention is usually used as a varnish which dissolved in the organic solvent. As an organic solvent which can be used here, it is the organic solvent of aliphatic series or an alicyclic ketone system, an ester system, and an ether system. When it forms a smooth paint film that the boiling point contains the organic solvent 100 degrees C or more among these, are desirable. as a ketone system A methyl n-pro building ketone, a diethyl ketone, a methyl isobutyl ketone, A methyl n-butyl ketone, an ethyl n-butyl ketone, a methyl n-amyl ketone, A diisobutyl ketone, a methyl n-hexyl ketone, a methyl oxide, a cyclohexanone, diacetone alcohol, a methyl phenol ketone, an isophorone; as an ester system n-propyl acetate, acetic-acid n-butyl, an isobutyl acetate, 2-methoxy ethyl acetate, Amyl acetate, an adipic-acid dimethyl, a glutaric-acid dimethyl, a succinic-acid dimethyl; as an ether system Propylene-glycol-monomethyl-ether acetate, such as methyl-cellosolve, 2-methoxy-2-propanol cellosolve, 1-ethoxy-2-propanol BUCHIRO cellosolve, 1, and 4-dioxane, is mentioned.

[0014]

[Example] Next, the example and the example of comparison of this invention are shown, and this invention is further explained to a detail.

60g of fluoride vinylidene system polymers which copolymerized 40 % of the weight of example 1 fluoride vinylidenes, 10 % of the weight of hexafluoropropylene, 40 % of the weight of tetrafluoroethylenes, and 10 % of the weight of 2-hydroxy ethylene allyl-compound ether, and 40g of vinyl system polymers which copolymerized 90 % of the weight of methyl methacrylate and 10 % of

the weight of methacrylic-acid 2-hydroxyethyl were dissolved in methyl-isobutyl-ketone 200g, and the polymer solution was obtained (50 mgKOH/g-dry). 50g of titanium oxide was put into this, and the ball mill was made to distribute with 1g of humid dispersants. To this, 30g [Japanese Polyurethane Industry] of isocyanate system curing agent coronate HL was added, and it painted in doctor grade so that it might become the thickness of 30 micrometers on an aluminum plate. The following examinations were performed after making it dry for seven days in ordinary temperature. [0015] (1) Resistance to solvents test toluene is included in a paper towel, rubbing of the paint film front face is carried out 100 times, and there are no abnormalities in the gloss of the rubbing section etc., or viewing estimated. (With no abnormalities;O, gloss fall,** of paint film, paint film dissolution;x)

(2) It is under a boiling-proof sex-test boiling water for 2 hours, and there are no abnormalities, such as a gloss fall, in a paint film, or viewing estimated. (With no abnormalities;O, gloss fall;x of paint film)

(3) It is the condition which carried out contamination-resistant test paint, performed 45 degree real exposure of 'south faces in Kawajiri-cho, Yokkaichi-shi, Mie-ken and the Ikejiri, Setagaya-ku, Tokyo town during four - October, 91, and became dirty about the dry sample board L* a*b* A color value and L* It asked for difference deltaL with the initial value of a value. (deltaL<10;O, 10<=deltaL<=20;** , deltaL>20;x)

As a result of evaluation, good and contamination-resistant deltaL of (3) was 10, and (1) solvent resistance and boiling-proof [(2)] nature were good.

[0016] Since it replaces with the curing agent of example 2 example 1 and printing dryness of Cymel 350 [Mitsui Cyanamid, Inc.] was carried out for 40g in addition 170 degrees C, and 20 minutes as an amino PURASUTSU compound system curing agent, it evaluated as well as the example 1.

(1) Solvent resistance, boiling-proof [(2)] nature, and the resistance to contamination by (3) real exposure were good.

[0017] It painted without putting a curing agent into example of comparison 1 example 1, and the same evaluation as an example 1 was performed.

(1) It was inferior to solvent resistance and boiling-proof [(2)] nature. (3) In real exposure, deltaL becomes 20 or more and is inferior to resistance to contamination.

[0018] Composition of the fluoride vinylidene system polymer of example of comparison 2 example 1 was replaced with 50 % of the weight of fluoride vinylidenes, 10 % of the weight of hexafluoropropylene, and 40 % of the weight of tetrafluoroethylenes, and was similarly estimated as the example 1.

(1) Gloss disappeared with solvent resistance.

(2) Gloss disappeared by boiling-proof nature.

(3) deltaL was 2.3 in resistance to contamination.

[0019] The same composition as the example 2 of comparison and composition of a vinyl system polymer were considered as the same composition as the example 3 of comparison, and composition of an example of comparison 3 fluoride vinylidene system polymer was similarly estimated as the example 1. Consequently, it was inferior by all evaluations.

[0020]

[Table 1]

比較例 3	50	10	40	—	90	—	10	—	—		x	x	△
例 2	0	0	0	—	0	0	—	0	—		△	x	x

組	成 (重量%)	実施例 1	実施例 2	比較例 1	比較
(A) 60g	フッ化ビニリデン	40	40	40	5
	ハキサフルオロプロピレン	10	10	10	1
	テトラフルオロエチレン	40	40	40	4
	ヒドロキシアリルエーテル	10	10	10	-
(B) 40g	メチルメタクリレート	90	90	90	9
	メタクリル酸ヒドロキシエチル	10	10	10	1
	メタクリル酸ブチル	—	—	—	-
	コロネートHL (g)	30	—	—	3
(C)	サイメカ350 (g)	—	40	—	-
評価項目					
(1) 耐溶剤性		○	○	×	
(2) 耐煮沸性		○	○	×	
(3) 耐汚染性		○	○	×	

[0021]

[Effect of the Invention] By having introduced the hydroxyl group as a bridge formation machine compared with the fluoride vinylidene system paint constituent currently used widely from the former, the fluoride vinylidene system paint constituent of this invention is excellent in solvent resistance and boiling-proof nature, is further improved greatly about the dirt of the paint film in real exposure, and has the performance which cannot become dirty easily from the conventional thing.

[Translation done.]